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(54) **Thermoplastic elastomeric composition**

(57) The thermoplastic elastomer composition is obtained by the steps of:(A) mixing (a) 10 to 70% by weight of a peroxide-degradable polyolefine; (b) 20 to 90% by weight of a peroxide-degradable polyolefine elastomer; (c) 0 to 60% by weight of a block copolymer having a structure of A-(B-A)<sub>n</sub>, wherein A is a block essentially consisting of a polymer of an aromatic vinyl compound; B is a block essentially consisting of a diene polymer; and (d) 0 to 50 parts by weight of a plasticizer, per 100 parts by weight of the total amount of the components (a), (b), and (c);(B) pelletizing the mixture;(C) melting and kneading the pellet with a peroxide at a temperature ranging from about 160°C to about 250°C for a sufficient time for a uniform composition. The composition gives a shaped article with excellent appearance upon a shaping step such as injection molding or extruding.

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Title of the Invention

## THERMOPLASTIC ELASTOMER COMPOSITION

Field of the Invention

5 The present invention relates to a thermoplastic elastomer composition mainly composed of polyolefine plastic and polyolefine elastomer, and especially related to a thermoplastic elastomer composition that can be molded into an article having a good appearance by injection-molding.

Background

10 Olefinic thermoplastic elastomers can be easily molded into an article having a complicated shape, therefore, olefinic thermoplastic elastomers are widely used for parts of automobiles, audio sets, television sets, video sets, or other.

There have been proposed many types of olefinic thermoplastic elastomers.

JP-B-53-34210 and JP-B-53-21021 show a thermoplastic elastomer consisting of a mono-olefinic copolymer rubber such as ethylene-propylene rubber and a polyolefinic plastic such as polypropylene.

15 JP-B-54-2662 discloses a thermoplastic elastomer comprising a mono-olefine copolymer rubber such as ethylene-propylene-diene terpolymer, and a crystalline polypropylene and/or a crystalline ethylene-propylene copolymer. According to the publication, the mono-olefine copolymer rubber and the crystalline polypropylene are previously mixed, and then, a cross-linking agent is incorporated and the mixture is kneaded to obtain a plastic elastomer.

JP-B-54-23702 discloses an elastomer comprising polyisobutylene and/or isoprene-isobutylene rubber, ethylene-propylene rubber and/or ethylene-propylene-diene rubber, and a poly- $\alpha$ -olefine such as polyethylene or polypropylene.

25 JP-B-56-15740, JP-B-56-15741, JP-B-56-15742, and JP-B-56-15743 disclose

another types of olefinic elastomer. These elastomers are obtained by kneading (a) peroxide-cross-linking olefinic rubber, i.e., an olefinic rubber that cross-links by heating with a peroxide, (b) a peroxide-degradable polyolefine i.e. an polyolefine that degrades by heating with a peroxide, (c) an elastomer that neither cross-links nor degrades by heating with a peroxide, such as a butyl rubber. These publication show ethylene-propylene rubber, ethylene-propylene-diene terpolymer, or ethylene-butadiene copolymer, as an example of component (a), and isotactic polypropylene, propylene-ethylene copolymer, or propylene-butene-1 copolymer are mentioned as an example of the component (b).

JP-B-62-10252 discloses an olefinic elastomer obtained by kneading (a) a previously cross-linked ethylene-propylene rubber and (b) an polyolefine.

JP-B-62-28977 discloses an elastomer comprising (a) a peroxide-cross-linking ethylene- $\alpha$ -olefine rubber such as ethylene-propylene rubber, ethylene-butene-1 rubber, ethylene-4-methylpentene-1 rubber, (b) a propylene- $\alpha$ -olefine rubber that neither cross-links nor degrades when heated with a peroxide, such as propylene-ethylene rubber or propylene- $\alpha$ -olefine rubber that has a propylene content of 55 to 80 mol%.

JP-B-62-59139 shows an elastomer comprising (a) peroxide cross-linking olefinic elastomer, (b) peroxide cross-linking polyolefine.

JP-B-01-22299 shows an elastomer for an automobile parts comprising a partially cross-linked olefinic rubber, a propylene-ethylene block copolymer, and an inorganic filler.

These elastomers have excellent elasticity, however, these elastomers hardly provide articles having excellent appearance, i.e. articles having no flow marks on their smooth surfaces.

#### Summary of the Invention

An object of the present invention is to provide an olefinic thermoplastic elastomer

which, upon a shaping step such as injection molding or extruding, gives an article having excellent appearance, i.e., an article having a smooth surface like a mirror and no flow marks. Instead of the smooth surface, some shaped articles may have a rough surface like a shark skin. The rough surface is caused when a surface of an injection mold is not accurately transposed to a thermoplastic elastomeric composition in the cavity. In the present invention, a "flow mark" refers to a stripe pattern on surface of a shaped article, especially by injection molding, which looks like a black stripe pattern like tiger's stripes.

The thermoplastic elastomer composition of the present invention comprises:

(a) 10 to 70% by weight of a peroxide-degradable polyolefine;

(b) 20 to 90% by weight of a peroxide-degradable polyolefine elastomer;

(c) 0 to 60% by weight of a block copolymer having a structure of A-(B-A)<sub>n</sub> (wherein A is a block essentially consisting of a polymer of an aromatic vinyl compound; B is a block essentially consisting of a diene polymer.);

(d) 0 to 50 parts by weight of a plasticizer, per 100 parts by weight of the total amount of the components (a), (b), and (c).

The thermoplastic elastomer can be obtained by kneading the components (a) and (b) or all of the component from (a) to (d) in the presence of a peroxide.

The peroxide reacts with the peroxide-degradable polyolefine and the peroxide-degradable polyolefine elastomer in the step of melting and kneading a mixture for a sufficient time to give a uniform composition. The temperature in the step of melting and kneading the mixture may be in a range of about 160° C and about 250° C, and preferably about 170° C and about 230° C.

#### Detailed Description of The Invention

The components (a), (b), (c) and (d) are mentioned in detail.

The component (a) is a peroxide-degradable polyolefine. A peroxide-degradable

polyolefine refers to a polyolefine which dominantly degrades into another polyolefine having a smaller molecular weight when the polyolefine is heated with a peroxide. When some polyolefines, which do not belong to the peroxide-degradable polyolefine are heated with the peroxide, the some polyolefines undergo cross linking to bridge main polymer chains rather than the degradation of the main polymer chains. Upon heating a polyolefine plastic or a polyolefine rubber with a peroxide, free radicals of a polyolefine chain generates so that the polyolefine chain breaks into a polyolefine chain having a shorter molecular weight or so that the polyolefine chain may form a chemical bonding with another polymer chain. The degradation reaction may happen in a polypropylene, and the cross linking reaction may happen in a polyethylene.

Polyolefines that can be employed as (a) the peroxide-degradable polyolefine are as follows:

Isotactic polypropylene, atactic polypropylene, syndiotactic polypropylene, ethylene-propylene block copolymer, ethylene-propylene random copolymer, propylene- $\alpha$ -olefine copolymer such as propylene-butene-1 copolymer, propylene-hexene-1 copolymer, propylene-4-methylpentene-1 copolymer, etc. Preferably, isotactic polypropylene, atactic polypropylene, syndiotactic polypropylene, ethylene-propylene block copolymer, and/or ethylene-propylene random copolymer may be used. Further preferably, isotactic polypropylene, and/or ethylene-propylene block or random copolymer having a propylene content of not less than 90 mol% may be used.

The polyolefines may be obtained by polymerizing propylene, ethylene, and/or  $\alpha$ -olefine with a Ziegler-Natta catalyst including a titanium halide, an organoaluminium compound, and, if necessary, a carrier such as magnesium chloride or silica. This preparation method is suitably for, for example, ethylene-propylene block copolymer, propylene-ethylene-propylene-block copolymer, etc.

The melt flow rate of the peroxide-degradable polyolefine is preferably from 3 to 50 g/10 min. A mixture of more than two polyolefines mentioned above can be used.

The component (b) is a peroxide-degradable polyolefine elastomer. A peroxide-degradable polyolefine elastomer is a polyolefine elastomer wherein degradation dominantly occurs when the elastomer is heated with a peroxide.

Polyolefine elastomers that can be used as the component (b) are as follows:

ethylene-propylene rubber having a propylene content of not less than 55 mol%, ethylene-propylene-diene terpolymer having a propylene content of not less than 55 mol%, elastomeric propylene- $\alpha$ -olefine copolymer such as a copolymer of 1-butene, 1-hexene, and/or a composition obtained by the polymerization of 4-methylpentene-1 and propylene.

The polyolefine elastomers may be obtained by polymerizing ethylene, propylene, and/or  $\alpha$ -olefine with a catalyst containing a vanadium compound and an organoaluminium compound or a catalyst containing a titanium compound and an organoaluminium compound.

A preferable catalyst may include: (a) a titanium complex containing Ti, Mg, a halogen, and an electron donor; (b) an organometallic compound of an element of the group 1, 2, or 12 of the Periodic Table; and (c), if necessary, an electron donor. JP-A-53-104687 discloses the catalyst.

The titanium complex may be obtained by a process including the steps of:

- (i) mixing a magnesium halide and an electron donor; and
- (ii) reacting the mixture with  $\text{TiCl}_4$ .

The mixing step may be performed in a mill.

The titanium complex may be obtained by another process including the steps of:

- (i) reacting a magnesium halide and an electron donor;

(ii) reacting the resulting product with an alkylaluminium compound, an organosilane, or an organohalosilane; and then

(iii) reacting the resulting mixture with  $\text{TiCl}_4$ .

The magnesium halide may include:

5       magnesium chloride, magnesium bromide, magnesium iodide, magnesium fluoride, anhydrous magnesium chloride, anhydrous magnesium bromide, and anhydrous magnesium fluoride. Among these, anhydrous magnesium chloride is preferable.

The electron donor may include:

10       alcohols having 1 to 18 carbon atoms such as methanol, ethanol, propanol, pentanol, hexanol, octanol, dodecanol, octadecylalcohol, benzyl alcohol, phenylethylalcohol, cumylalcohol, isopropylbenzylalcohol, and any combinations thereof;

phenols having 6 to 15 carbon atoms such as phenol, cresol, xylene, ethylphenols, propylphenols, cumylphenol, naphthols, and any combinations thereof;

15       ketones having 3 to 15 carbon atoms such as acetone, methyl ethyl ketone, methyl isobutyl ketone, acetophenone, benzophenone, cyclohexanone, benzoquinone, and any combinations thereof;

aldehydes having 2 to 15 carbon atoms such as acetaldehyde, propionaldehyde, octylaldehyde, benzaldehyde, naphthylaldehyde, and any combinations thereof;

20       ethers having 2 to 18 carbon atoms such as methyl formate, methyl acetate, vinyl acetate, vinyl crotonate, vinyl propionate, octyl acetate, cyclohexyl acetate, ethyl propionate, methyl butyrate, ethyl valerate, ethyl chloroacetate, ethyl dichloroacetate, methyl methacrylate, methyl crotonate, ethyl cyclohexanate, methyl benzoate, ethyl benzoate, propyl benzoate, butyl benzoate, octyl benzoate, cyclohexyl benzoate, phenyl benzoate, benzyl benzoate, methyl toluylate, ethyl toluylate, amyl  
25       toluylate, ethyl ethylbenzoate, methyl anisate, ethyl anisate, ethyl ethoxybenzoate,  $\gamma$ -

butylolactone,  $\delta$ -valerolactone, coumarin, phthalide, ethylene carbonate and any combinations thereof;

acid halides having 2 to 15 carbon atoms such as acetyl chloride, benzyl chloride, toluyl chloride, anis chloride and any combinations thereof;

5 ethers having 2 to 20 carbon atoms such as methyl ethers, ethyl ethers, isopropyl ethers, butyl ethers, amyl ethers, ketohydrofuran, anisole, diphenylether and any combinations thereof;

amidos such as acetoamide, toluylamido, benzoamido;

amines such as methyl amine, ethyl amine, diethyl amine, tributyl amine, piperidine, 10 tribenzyl amine, aniline, pyridine, picoline, tetramethylethylenamine and any combinations thereof; and

nitriles such as acetonitrile, benzonitrile, tolunitrile and any combinations thereof.

The organometallic compound includes trialkylaluminium, dialkylaluminium hydride, alkylaluminium dihydride, alkylaluminium alkoxide, dialkylaluminium halide, 15 alkylaluminium dihalide, dialkylzink, dialkylmagnesium.

A mixture of any of the combinations of the polyolefine elastomers mentioned above can be used.

The component (c) is a block copolymer having a structure of  $A-(B-A)_n$ , wherein A is a block of polymer of an aromatic vinyl compound such as styrene,  $\alpha$ -methyl 20 styrene, and/or chlorostyrene and B is a block of a polymer of a conjugated diene such as butadiene, isoprene, chloroprene, or other. 'n' indicates an integer ranging from 1 to 5.

A block polymer obtained by hydrogenating the copolymer mentioned above also can be used as the component (c).

25 Styrene-butadiene-styrene block polymer, styrene-isoprene-styrene block polymer,

hydrogenated styrene-butadiene-styrene block polymer, and hydrogenated styrene-isoprene-styrene block polymer are the most preferable block copolymer used as the component (c).

The component (d) is a plasticizer. Extender oil, and processing oil, both of which were commonly used in rubber industry can be preferably used as the component (d).

5 Particularly paraffin oil, nephtenic oil, and aromatic oil can be used preferably.

The amount of each component is as follows.

The amount of the component (a) is 10 to 70% by weight, preferably, 20 to 60% by weight. A thermoplastic elastomer composition having a content of the component (a) of less than 10% by weight has inferior tensile strength, low elongation, and low softening  
10 temperature. Such thermoplastic elastomer composition gives an article having many flowmarks on the surface by injection molding. In contrast, a thermoplastic elastomer composition having a content of the component (a) of more than 70% by weight has no elasticity.

The amount of the component (b) is 20 to 90% by weight, preferably, 40 to 70%  
15 by weight. A thermoplastic elastomer composition having a content of the component (b) of less than 20% by weight has poor mechanical properties and low softening temperature. Such thermoplastic elastomer composition also give an article having many flowmarks on the surface. In contrast, a thermoplastic elastomer composition having a content of the component (a) of more than 90% by weight is not preferable, too, because such  
20 thermoplastic elastomer composition cross-links too much when kneaded under the existence of a peroxide.

The amount of the component (c) is not more than 60% by weight, preferably not more than 50% by weight. A thermoplastic elastomer composition having a content of the component (c) of more than 60% by weight provide an article having flowmarks  
25 through injection molding.

The thermoplastic elastomer composition of this invention has a content of the component (d) of not more than 50 parts by weight, per 100 parts by weight of the total amount of the components (a) to (c). A thermoplastic elastomer having a content of the component (d) of more than 50% by weight has a problem that the component (d) exude  
5 to surface of an article molded from the composition.

The thermoplastic elastomer composition of the present invention can incorporate an inorganic filler such as carbon black, calcium carbonate, calcium silicate, clay, kaolin, talc, silica, alumina, titanium oxide, red iron oxide, zinc oxide, barium sulfate, aluminum sulfate, calcium sulfate, alkaline magnesium carbonate, glass powder, kieselguhr, mica  
10 powder, and/or asbestos powder.

Inorganic pigments such as ultramarine, prussian blue, cobalt oxide, chrome yellow, cadmium yellow, red lead, lithophone, titanium white, zinc white, yellow iron oxide, iron black can be incorporated to the composition.

Organic pigments such as lake pigments or phthalocyanine pigments also can be  
15 incorporated to the composition.

Antioxidant and/or light stabilizer can be added.

The thermoplastic elastomer composition of the present invention can be provided by kneading the composition (a), (b), if necessary, (c) and (d) in the presence of a peroxide.

20 The components (a), (b), (c), (d), and the peroxide can be mixed and kneaded at one time.

Another process having the steps of:

(A) mixing the components (a), (b), (c), and (d);

(B) pelletizing the mixture;

25 (C) putting the peroxide on the pellet; and then,

(D) melting and kneading the pellet

can give the composition of the present invention.

The amount of the peroxide is preferably 0.02 to 1.00 parts by weight and preferably 0.05 to 0.5 parts by weight per 100 parts by weight of the total amount of the components (a), (b), (c), and (d).

When less than 0.02 parts by weight of the peroxide is incorporated, the resultant thermoplastic elastomer composition does not provide an article having an excellent appearance by injection molding. On the other hand, when more than 1.00 parts by weight of the peroxide is incorporated, the resultant thermoplastic elastomer composition does not have an excellent mechanical property.

The peroxide that can be preferably used is as follows:

dicumenyl peroxide, di-tert-butylperoxide, 2,5-dimethyl-2,5-di-tert-butylperoxy)hexane, 2,5-dimethyl-2,5-di-(tert-butylperoxy)hexane-3, 1,3-bis(tert-butylperoxyisopropyl)benzene, 1,1-bis(tert-butylperoxy)-2,3,5-trimethylcyclohexane, n-butyl-4,4'-bis(tert-butyl) valerate, benzoyl peroxide, 2,4-dichlorobenzoyl peroxide, tert-butyl peroxybenzoate, tert-butyl peroxyisopropylcarbonate, diacetyl peroxide, lauroyl peroxide, tert-butyl cumenyl peroxide, etc.

A mixture of the peroxides shown above also can be used.

An accelerator for cross-linking can be incorporated with the peroxide. The accelerator includes such as divinyl benzene, sulfur, p-quinonedioxime, p,p'-dibenzoylquinonedioxime, N-methyl-N,6-dinitrosoaniline, nitrobenzene, diphenylguanidine, triarylcyaurate, trimethylolpropane-N,N'-m-phenylenedimaleimide, ethyleneglycol dimethacrylate, polyethylene dimethacrylate, trimethylolpropane trimethacrylate, arylmethacrylate, vinylbutylate, and vinylstearate.

The amount of the accelerator is 0.02 to 2.00 parts by weight per 100 parts by

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weight of the total amount of the components (a), (b), (c) and (d).

A kneading machine may be used for melting and kneading the components, and the kneading machine includes a kneader, a Banbury mixer, an extruder, a continuous kneader, a roll mill, a taper roller, etc. The extruder is preferable.

### EXAMPLES

#### 5 (Injection Molding)

In working examples and comparative examples, each of thermoplastic elastomer compositions underwent injection molding to shape a plate having dimensions of 360 mm and 140 mm and a thickness of 3 mm, and then the plate was visually inspected for presence of flow marks and surface smoothness. An injection molding machine having  
10 a commercial name of UBE MAX 10 OUNCES from UBE Industries Ltd. was used.

Experimental conditions for the injection molding is as follows:

an injection pressure was 840 kgf/cm<sup>2</sup>;

an injection temperature ranges from 180°C to 200°C;

a temperature of an injection mold was preheated to 40°C;

15 a size of the injection mold was 360mm x 140 mm x 3 mm; and

the injection mold has a one-point gate at its side;

wherein 1 kgf is equivalent to 9.81 N.

#### (Testing Methods)

##### (1) Melt Flow Rate (MFR)

20 A melt flow rate was measured at 230°C with a load of 2.160 kgf, following the method specified in ASTM D1238.

##### (2) Hardness

A hardness of the plate which was shaped by the injection molding under conditions above was measured, following the method specified in JIS K6301, wherein JIS stands for  
25 Japan Industrial Standard.

(3) Tensile strength and Elongation upon tensile force

The plate which was shaped by the injection molding under conditions above was blanked so as to give a blank having a shape of a dumbbell of size 3. A tensile strength of the blank, which was used as a test piece, was measured under conditions of a tensile speed of 500 mm per minute and an interval of 20 mm, following the method specified in JIS K6301.

(4) Compressive Permanent Strain

The plate which was shaped by the injection molding under conditions above was blanked so as to give four blanks. The four blanks were laminated, and a compressive permanent strain of the four laminated blanks were measured under conditions of 70° C, 22 hours, and deformation of 25%. The measurement followed the method specified in JIS K6301.

(5) Softening Point

A softening point was measured, following the method for measuring a Bicket softening point specified in JIS K7206.

(6) Appearance of Shaped Plate

The plate which was shaped by the injection molding under the conditions above was visually inspected for surface smoothness and the presence of flow mark. Appearance of the shaped plate was evaluated on the basis of the standards as follows:

When the plate has a smooth surface like a mirror or the plate has a minute portion of its surface like a rough surface like a shark skin, the plate surface smoothness is satisfactory and the column of "smoothness" in Table 1 is indicated as "o". In the contrary, when the plate clearly has a portion of a rough surface like a shark skin by the visual inspection, an appearance for the smoothness is failure and indicated as "x" in Table 1.

When the flow mark is not present at all or only a minute flow mark is present on the surface of the plate by the visual inspection, an appearance for the flow mark is satisfactory and indicated as "o" in the column of flow mark in Table 1. In the contrary, when any flow mark was clearly present on surface of the plate by the visual inspection, an appearance for the flow mark is failure and indicated as "x" in the column of flow mark in Table 1.

(EXAMPLES 1-8; COMPARATIVE EXAMPLES 1-4)

Constitutions of starting materials for Examples 1-8 and Comparative Examples 1-4 are summarized in Table 1. The same component is used for all of the Examples and the Comparative Examples.

Components in the Examples and Comparative Examples are as follows:

PP in the Table stands for a PolyPropylene composition, and a block copolymer of ethylene and propylene (i.e., an ethylene-propylene block copolymer) having a commercial name under J703H from UBE INDUSTRIES LTD. was used. The block copolymer has a melt flow rate of 3 gram per 10 minutes, and contains 4% by mole of ethylene units.

EPR-1 in the Table stands for an Ethylene-Propylene Rubber having a commercial name of TAFUMER-S-4030 from MITSUI PETROCHEMICAL LTD. (MITSUI SEKIYU KAGAKU LTD.) was used. The rubber has a melt flow rate of 0.4 gram per 10 minutes, and contains 59% by mole of propylene units.

EPR-2 in the Table stands for an Ethylene-Propylene Rubber having a commercial name of EPO7P from JAPAN SYNTHETIC RUBBER LTD. was used. The rubber has a Mooney viscosity  $ML_{1+4}$  at 100° C of 70, and contains 27% by mole of propylene units.

SEPS in the Table stands for a Styrene-Ethylene-Propylene-Styrene block copolymer having a commercial name of SEPTON2005 from CHLARE LTD. (KURARE LTD.) was

used. The block copolymer was hydrogenated, and contains 20% by weight of styrene units. The block copolymer has a number average molecular weight of about 190,000.

The plasticizer in Table 1 refers to a paraffin oil having a commercial name of DYNAPROCESS OIL PW-90. The paraffin oil has a kinematic viscosity at 40° C of 95.54 cSt, and an average molecular weight of 539.

The peroxide in Table 1 has a commercial name of PERHEXA 2.5B from NIHON YUSHI LTD.

Divinylbenzene in Table 1 is used as an accelerating agent for cross linking.

In any of the Examples and the Comparative Examples, an amount of each of the plasticizer, the peroxide, and the divinylbenzene is expressed by parts by weight per 100 parts by weight of the total amount of the PP, the EPR-1, the EPR-2, and the SEPS.

In any of the Examples and the Comparative Examples, the PP, the EPR-1, the EPR-2, the SEPS, the plasticizer, and the divinylbenzene were mixed together by a tumbler blender to give a mixture; and then melting and kneading the mixture at 200° C by a twin screw extruder having a commercial name of UME 44 from UBE INDUSTRIES LTD. so as to give a plurality of pellets. In the latter step of melting and kneading the mixture, the screw rotated 200 cycles per minute, and a nitrogen gas was flowing through a lower portion in the hopper of the extruder.

The pellets were mixed with the peroxide by the tumbler blender, and the mixture was melted and kneaded at 200° C by the twin screw extruder to give a thermoplastic composition. The peroxide reacts with the polypropylene composition, the EPR-1 and the EPR-2 during the step of melting and kneading the mixture.

The thermoplastic elastomer composition was shaped by the aforementioned injection molding to give the plate, and aforementioned properties of the plate were measured. The result is summarized in Table 1.

As is readily apparent from the above description, additional advantages and modifications will readily occur to one skilled in the art. The invention in its broader aspects is therefore not limited to the specific examples shown and described. Accordingly, departures may be made from the details shown in the example without departing from the spirit or scope of the disclosed general inventive concept.

TABLE 1

		E x a m p l e								Comparative Example			
		1	2	3	4	5	6	7	8	1	2	3	4
Composition	PP (wt%)	40	20	20	30	40	40	40	20	40	40	5	20
	EPR-1 (wt%)	40	40	70	50	50	20	60	30	40	20	50	19
	EPR-2 (wt%)	0	0	0	0	0	0	0	0	0	20	0	0
	SEPS (wt%)	20	40	10	20	10	40	0	50	20	20	45	61
	Plasticizer (weight parts)	30	50	30	30	15	30	30	30	30	0	30	30
	Peroxide (weight parts)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0	0.2	0.2	0.2
Divinyl benzene (weight parts)	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0	0.3	0.3	0.3	
	Hardness	86	68	75	80	90	87	86	71	87	85	55	48
Tensile Strength (kg/cm <sup>2</sup> )		58	35	54	55	68	62	49	69	64	65	21	32
Tensile Elongation (%)		530	560	510	530	590	550	480	620	570	350	390	420
Compressive Permanent Strain (%)		55	47	55	52	52	60	54	64	52	73	74	68
Softening Point (°C)		131	102	115	125	140	140	123	125	129	139	74	65
Appearance	Smoothness	0	0	0	0	0	0	0	0	0	x	x	x
	Flow Mark	0	0	0	0	0	0	0	0	x	x	x	x

o is satisfactory  
x is failure

WHAT WE CLAIM IS:

1. A thermoplastic elastomer composition comprising:

(a) 10 to 70% by weight of a peroxide-degradable polyolefine;

(b) 20 to 90% by weight of a peroxide-degradable polyolefine elastomer;

5 (c) 0 to 60% by weight of a block copolymer having a structure of  $A-(B-A)_n$ ,

wherein A is a block essentially consisting of a polymer of aromatic vinyl units, and B is a block essentially consisting of a polymer of diene units;

(d) 0 to 50 parts by weight of a plasticizer, per 100 parts by weight of the total amount of the components (a), (b), and (c);

10 wherein the thermoplastic resin is obtained by mixing the components (a), (b), (c) and (d) with a peroxide.

2. A thermoplastic elastomer composition of claim 1, wherein an amount of the peroxide-degradable polyolefine is 20 to 60% by weight.

3. A thermoplastic elastomer composition of claim 1, wherein an amount of the peroxide-degradable polyolefine elastomer is 40 to 70% by weight.

4. A thermoplastic elastomer composition of claim 1, wherein an amount of the block copolymer is not more than 50% by weight.

5. A thermoplastic elastomer composition of claim 1, wherein the amount of the peroxide is 0.02 to 1.00 parts by weight per 100 parts of the total amount of the components (a), (b), (c) and (d).

6. A thermoplastic elastomer composition of claim 1, wherein the peroxide-degradable polyolefine comprises at least one of polypropylene, ethylene-propylene copolymer, and propylene- $\alpha$ -olefine copolymer.

7. A thermoplastic elastomer composition of claim 6, wherein the propylene- $\alpha$ -olefine copolymer comprises at least one of the group consisting of propylene-1-butene block

copolymer, propylene-1-butene random copolymer, propylene-1-hexene block copolymer, propylene-1-hexene random copolymer, propylene-4-methylpenten-1 block copolymer, and propylene-4-methylpenten-1 random copolymer.

8. A thermoplastic elastomer composition of claim 7, wherein the peroxide-degradable polyolefine comprises at least one of isotactic polypropylene, atactic polypropylene, ethylene-propylene block copolymer containing 90 mol% or more of propylene, and ethylene-propylene random copolymer containing 90 mol% or more of propylene.

9. A thermoplastic elastomer composition of claim 1 wherein the peroxide-degradable polyolefine elastomer comprises at least one of the group consisting of ethylene-propylene rubber containing at least 55 mol% of propylene units, ethylene-propylene-diene rubber containing at least 55 mol% of propylene units, and amorphous propylene- $\alpha$ -olefine copolymer.

10. A thermoplastic elastomer composition of claim 9 wherein the peroxide-degradable polyolefine elastomer comprises at least one of ethylene-propylene rubber containing at least 55 mol% of propylene units, ethylene-propylene-diene rubber containing 55 mol% or more of propylene, and an amorphous copolymer composition prepared from propylene and at least one of the group consisting of 1-butene, 1-hexene, and 4-methylpentene-1.

11. A thermoplastic elastomer composition of claim 1 wherein A of the block copolymer essentially consists of one of the group of a polymer of styrene,  $\alpha$ -methylstyrene, ethylstyrene, and chlorostyrene and B of the block copolymer essentially consists of one of polybutadiene, polyisoprene, polyethylene, polypropylene, and poly- $\alpha$ -olefine.

12. A thermoplastic elastomer composition of claim 1 wherein the block copolymer comprises at least one of styrene-butadiene-styrene block copolymer, styrene-isoprene-styrene block copolymer, hydrogenated styrene-butadiene-styrene block copolymer, and hydrogenated styrene-isoprene-styrene block copolymer.

13. A process for producing a thermoplastic elastomer composition by mixing:

(a) 10 to 70% by weight of a peroxide-degradable polyolefine;

(b) 20 to 90% by weight of a peroxide-degradable polyolefine elastomer;

(c) 0 to 60% by weight of a block copolymer having a structure of  $A-(B-A)_n$ ,

5 wherein A is a block essentially consisting of a polymer of aromatic vinyl units, and B is a block essentially consisting of a polymer of diene units; and

(d) 0 to 50 parts by weight of a plasticizer, per 100 parts by weight of the total amount of the components (a), (b), and (c);

in the presence of a peroxide.

10 14. A process of claim 13 comprising the steps of:

(A) mixing the components (a), (b), (c), and (d);

(B) pelletizing the mixture;

(C) putting the peroxide on the pellet; and then,

(D) melting and kneading the pellet.

15 15. A process of claim 13 or 14 wherein an accelerator is incorporated during mixing or kneading.

16. A process of claim 15 wherein the accelerator is at least one compound selected from the group of divinyl benzene, sulfur, p-quinonedioxime, p,p'-dibenzoylquihoneoxime, N-methyl-N,6-dinitrosoaniline, nitrobenzene, diphenylguanidine, triarylcyanurate, trimethylolpropane-N,N'-m-phenylenedimaleimide, ethyleneglycol dimethacrylate, polyethylene dimethacrylate, trimethylolpropane trimethacrylate, arylmethacrylate, vinylbutylate, and vinylstearate, is incorporated as a cross-linking accelerator.

20 17. A process of claim 15 or 16 wherein the amount of the accelerator is 0.02 to 2.00 parts by weight per 100 parts by weight of the total amount of the components (a), (b),  
25 (c) and (d).

18. A thermoplastic elastomer composition produced by a method comprising a step of:  
melting and kneading a mixture having:

(a) 10 to 70% by weight of a peroxide-degradable polyolefine;

(b) 20 to 90% by weight of a peroxide-degradable polyolefine elastomer;

5 (c) 0 to 60% by weight of a block copolymer having a structure of  $A-(B-A)_n$ ,

wherein A is a block essentially consisting of a polymer of aromatic vinyl units, and B  
is a block essentially consisting of a polymer of diene units; and

(d) 0 to 50 parts by weight of a plasticizer, per 100 parts by weight of the total  
amount of the components (a), (b), and (c); and

10 (e) a peroxide

at a temperature ranging from about 160° C to about 250° C for a sufficient time for  
a uniform composition.

**Relevant Technical Fields**

(i) UK CI (Ed.L) C3M (MD, MXC)

(ii) Int CI (Ed.)

**Databases (see below)**

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

(ii) ONLINE DATABASES: WPI

Search Examiner  
 K MACDONALD

Date of completion of Search  
 15 DECEMBER 1993

Documents considered relevant  
 following a search in respect of  
 Claims :-  
 1-18

**Categories of documents**

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| <p><b>X:</b> Document indicating lack of novelty or of inventive step.</p> <p><b>Y:</b> Document indicating lack of inventive step if combined with one or more other documents of the same category.</p> <p><b>A:</b> Document indicating technological background and/or state of the art.</p> | <p><b>P:</b> Document published on or after the declared priority date but before the filing date of the present application.</p> <p><b>E:</b> Patent document published on or after, but with priority date earlier than, the filing date of the present application.</p> <p><b>&amp;:</b> Member of the same patent family; corresponding document.</p> |
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Category	Identity of document and relevant passages	Relevant to claim(s)
	NONE	

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